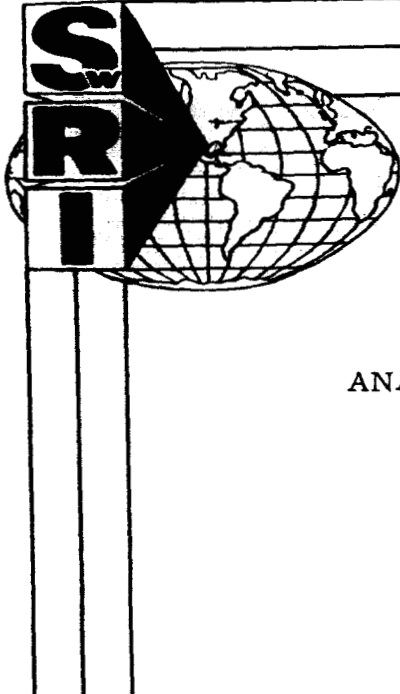


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Herbert C. McKee
William A. McMahon

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to

NASA Manned Spacecraft Center
Propulsion and Power Division
Houston, Texas 77058

April 15, 1966

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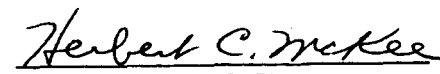
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APPROVED BY:


Herbert C. McKee
Assistant Director
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SOUTHWEST RESEARCH INSTITUTE

I. INTRODUCTION

This investigation was undertaken to develop methods of trace analysis and to measure impurities in samples of nitrogen tetroxide (N_2O_4). This was done to see if variations in trace impurities in different samples of N_2O_4 might be related to the pattern of stress corrosion in titanium alloy tanks used for this material.

Four samples of N_2O_4 were furnished by the sponsor, from the following sources:

1. North American
2. NASA Manned Spacecraft Center
3. Bell Aerosystems
4. Hercules

Originally, it was anticipated that approximately one gram of residue could be obtained by the evaporation of approximately one liter of sample, thus providing ample material for analysis by a variety of methods. It was found, however, that the amount of residue was considerably less, averaging no more than 10 to 20 milligrams per liter. This made it impossible to complete the analytical work originally anticipated, and also made it less likely that trace impurities in the material might account for the differences in corrosion characteristics.

After preliminary work had confirmed the small amount of residue in the samples, the scope of the study was changed to conduct most of the analytical work on nitrogen tetroxide rather than on the residue, and additional emphasis was placed on determining nitric oxide (NO), since some evidence existed that the amount of nitric oxide might be important in determining the corrosion patterns. In addition, a method was developed to determine nitric oxide in N_2O_4 using a mass spectrometer. This was accomplished by some modification of the inlet system on the instrument and by the development of suitable handling techniques, and it is felt that the method which is now available is adequate for the purposes intended.

II. SAMPLE HANDLING

Because of the highly reactive nature of N_2O_4 , special procedures were required in handling the samples prior to analysis. The samples were delivered in stainless steel pressure cyclinders equipped with stainless steel valves and fittings. All handling had to be accomplished under a nitrogen atmosphere in order to avoid contact with atmospheric moisture which would cause rapid reaction and contamination of the samples. This was accomplished by fitting a 1/16 inch O. D. stainless steel delivery line on each cyclinder and using this to transfer small amounts of sample into various sample containers for subsequent analysis. All materials contacting the N_2O_4 samples were either stainless steel or glass.

Evaporation tests were first conducted to determine the amount of nonvolatile residue present in the samples. For this purpose, 100 ml portions of N_2O_4 were placed in a clean, dry flask maintained under a nitrogen atmosphere. Continued purging with dry nitrogen removed the vapor which boiled off of the sample. A small amount of heat was supplied to maintain the temperature near room temperature and facilitate evaporation. If purging was not adequate, moisture formed in the bottom of the flask indicating contamination with water vapor. However, with careful technique and continued purging, it was possible to evaporate all the sample without introducing water. When this was done, it was found that the amount of residue obtained was in the range of 10 to 20 milligrams per liter. Therefore, a decision was made to conduct analytical work with N_2O_4 rather than with the residue since the amount of residue was too small to permit analysis as originally anticipated.

After some further experimentation, the following procedure was developed to remove small samples from the pressure containers and contain them for analysis:

The sample container was clamped into an upright position and fitted with a coil of 1/8 inch stainless steel tubing which was immersed in a Dewar flask filled with ice water. After emerging from the ice bath, the tubing was fitted with a reducer union so that the delivery of the sample at the exit was from a 1/16 inch stainless steel tube. The sampling system was cleaned with nitric acid, distilled water, and dried with N_2 before use and between sample bombs.

All five samples were taken in sequence as described below:

1. Approximately 100 ml of N_2O_4 was delivered into a 200 ml beaker to purge out and cleanse the sampling system. This N_2O_4 was discarded. Immediately after sampling, the delivery tip was wiped with a "bay wipe" and inserted into a test tube equipped with a rapid dry nitrogen purge.
2. A second 100 ml of sample was delivered into a clean dry 200 ml beaker and this was allowed to evaporate in the open air so as to leave a small quantity of nitric acid residue. This residue was then sealed into a length of 8 mm glass tubing for transport to the emission spectrograph laboratory.
3. Three small samples were then taken for ESR, NMR, and mass spectrometer analysis. The standard quartz sample tubes were utilized for ESR and NMR and an 8 inch length of 8 mm glass tubing for the mass spectrometer sample. In collecting these samples, the tubes were purged with dry nitrogen via a stainless steel capillary tube and the N_2O_4 delivered to the tube while purging continued. The samples were frozen with dry ice under nitrogen purge and then quickly sealed off with an oxygen torch. (In taking these samples, the tip was cleaned and a small amount of N_2O_4 delivered first to waste with a nitrogen purge prior to insertion into the sample tubes.)
4. "Residue" samples were collected in 250 ml Erlenmeyer flasks with 24/40 joints for the neck. A gas inlet tube was utilized to stopper the flask, supply the nitrogen purge (to exclude air and H_2O), and vent the N_2O_4 vapor. 100 ml samples of N_2O_4 were taken. Weighable samples of residue were not obtained with the MSC and Hercules samples. Approximately 0.3 ml of a liquid (appeared to be concentrated nitric acid) was obtained from the Bell Systems and North American samples. It was not possible to get a weight on the quantity of residue since it was not entirely possible to determine at what point the residue was liquid N_2O_4 or concentrated nitric acid. Since all four samples were handled by identical methods, it is thought that the residues from the Bell and North American samples resulted from water originally present in the N_2O_4 , and not from water introduced in sample handling.

The same method was used to fill the special sample containers which were ultimately used for mass spectrometer analysis, as will be described later in this report.

III. ANALYTICAL RESULTS

This section of the report discusses the various analytical techniques that were used and the results obtained.

A. Nuclear Magnetic Resonance

Nuclear magnetic resonance is a technique which measures nuclear spin phenomena in order to obtain information on isotope composition and molecular structure. A particular useful form involves measurement of protons or hydrogen atoms, to determine the molecular structure within which they occur. Such measurements are especially useful to identify the molecular structure of various organic compounds, and nuclear spin resonance was originally included in the investigation as a possible means of identifying any organic compounds in the residue. Since the amount of residue was too small to permit this, measurements were made on the N_2O_4 itself rather than on a residue, which resulted in a decrease in sensitivity so far as organic impurities were concerned.

NMR spectra were determined for the four N_2O_4 samples, using a Varian A-60 spectrometer scanned from 0-10.0 ppm at room temperature. TMS was used as the standard to determine the 0 ppm line but it could not be used as an internal standard because of the nature of the samples. In addition, the residues from the Bell Systems and North American samples were evaporated and spectra determined.

All six samples exhibit one absorption between 8.5 and 11.0 ppm which is probably from water protons in a highly electronegative environment such as would be provided by NO_2 . It would be necessary to introduce an internal standard to determine any variations from one sample to the next. However, the two residues indicated much higher concentrations of water, confirming the tentative identification of these residues as concentrated nitric acid.

ESR studies indicated the presence of several paramagnetic substances in the N_2O_4 samples. These paramagnetic substances made it very difficult to interpret NMR spectra recorded in their

presence. Since mass spectrometer data were expected to provide better information on NO (and therefore water), no further attempt was made with NMR. No organic constituents were indicated by the NMR spectra.

B. Electron Spin Resonance

This technique is sensitive to unpaired electrons and thus provides information on paramagnetic material in the sample. It is particularly useful in identifying organic free radicals and thus providing information on certain organic reactions which proceed by a free radical mechanism. As with NSR, however, working with the original N_2O_4 rather than with residue limited the sensitivity which could be obtained.

The four samples of N_2O_4 were scanned in the Varian ESR spectrometer at room temperature and the signals were all the same. This was a large broad signal centered about $g = 2.0$ which is due to the large concentration of NO_2 at room temperature. A typical ESR spectrum is shown in Figure 1.

The samples were frozen slowly with dry ice in an attempt to drive the chemical equilibrium to the N_2O_4 side of the reaction $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$. After the samples had reached -78°C , they were immersed in liquid nitrogen and again scanned, this time at -196°C . The ESR spectrum obtained was much smaller and showed hyper-fine structure. However, analysis of the structure proved it to be NO_2 again. A typical ESR spectrum of the NO_2 at -196°C is shown in Figure 2. The splitting of the lines was found to be orientation dependent but no species other than NO_2 could be identified. All four samples produced similar ESR spectra, the only differences being caused by differences in freezing rates and orientation of the sample in the magnetic field.

The two liquid residue samples mentioned previously were also scanned. These were liquid residues from the evaporation (under nitrogen) of the Bell Systems and North American samples, and appeared to be nitric acid. These samples were frozen in liquid nitrogen and maintained at -196°C during scanning. The spectra obtained from these samples are shown in Figures 3 through 6. The broad scans show that the Bell sample has a

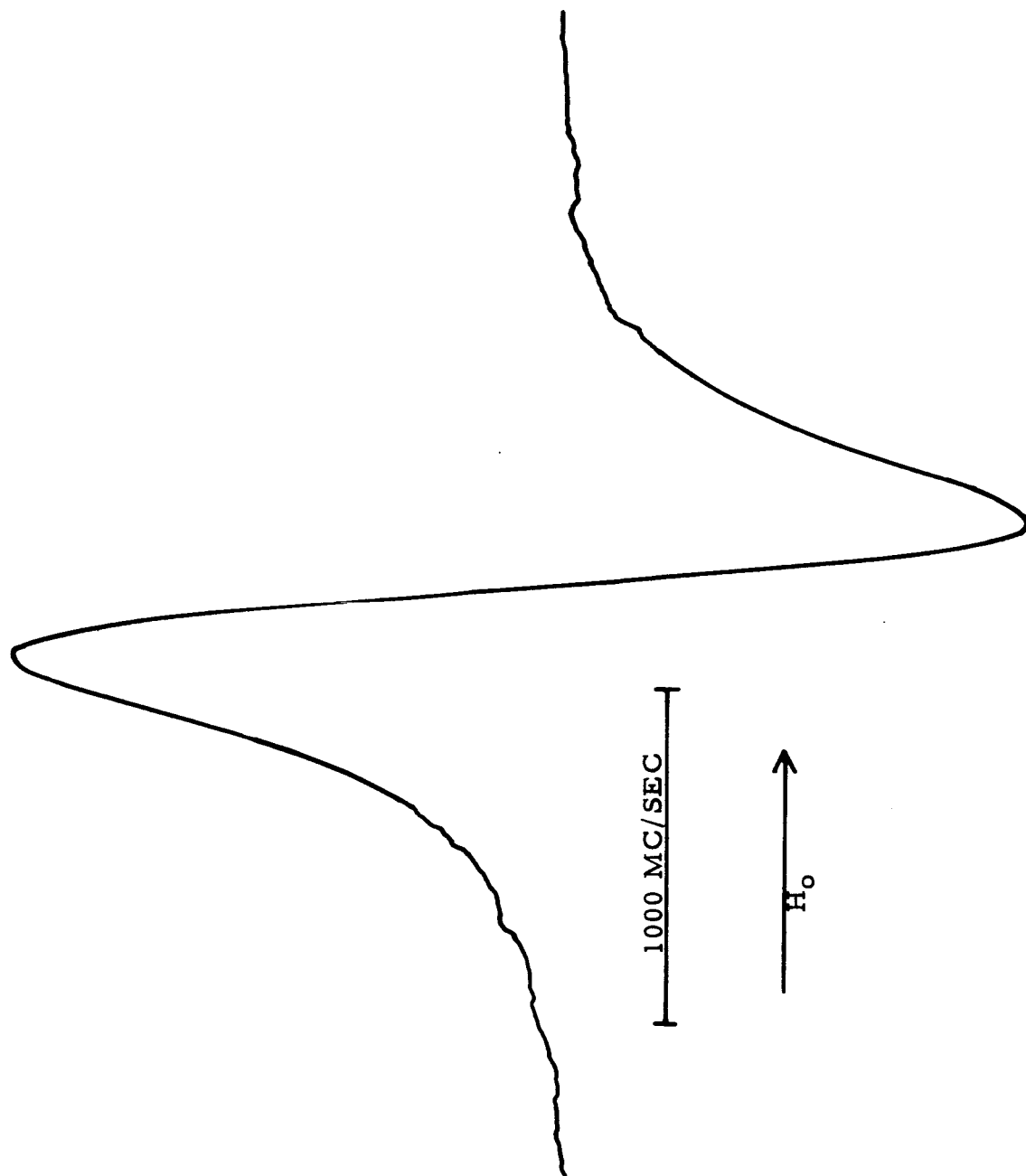


FIGURE 1. TYPICAL ESR SPECTRUM OF N_2O_4 SAMPLE AT ROOM TEMPERATURE

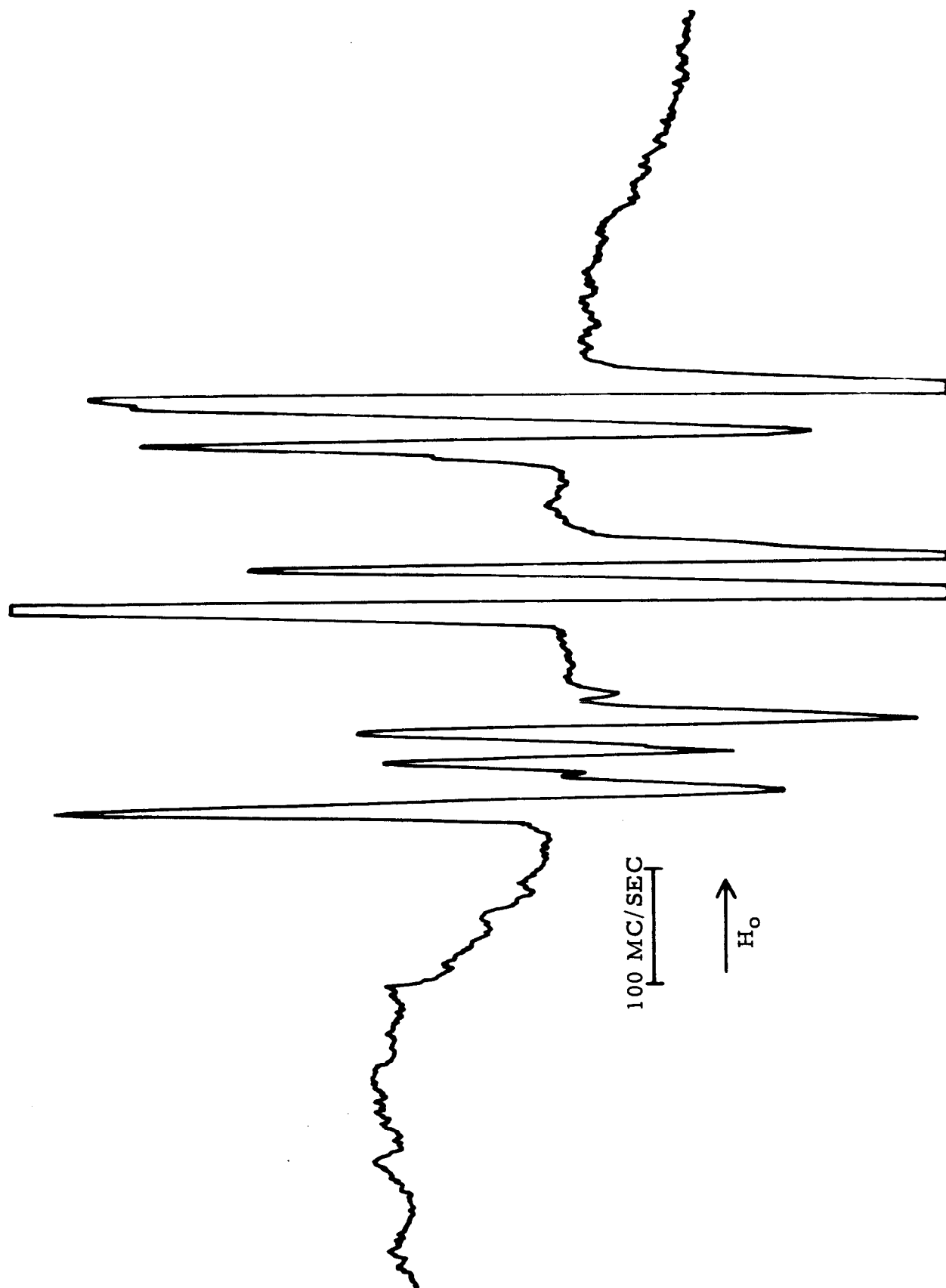


FIGURE 2. TYPICAL ESR SPECTRUM OF N_2O_4 SAMPLE SHOWING NO_2 HYPERFINE SPLITTING AT $-196^\circ C$.

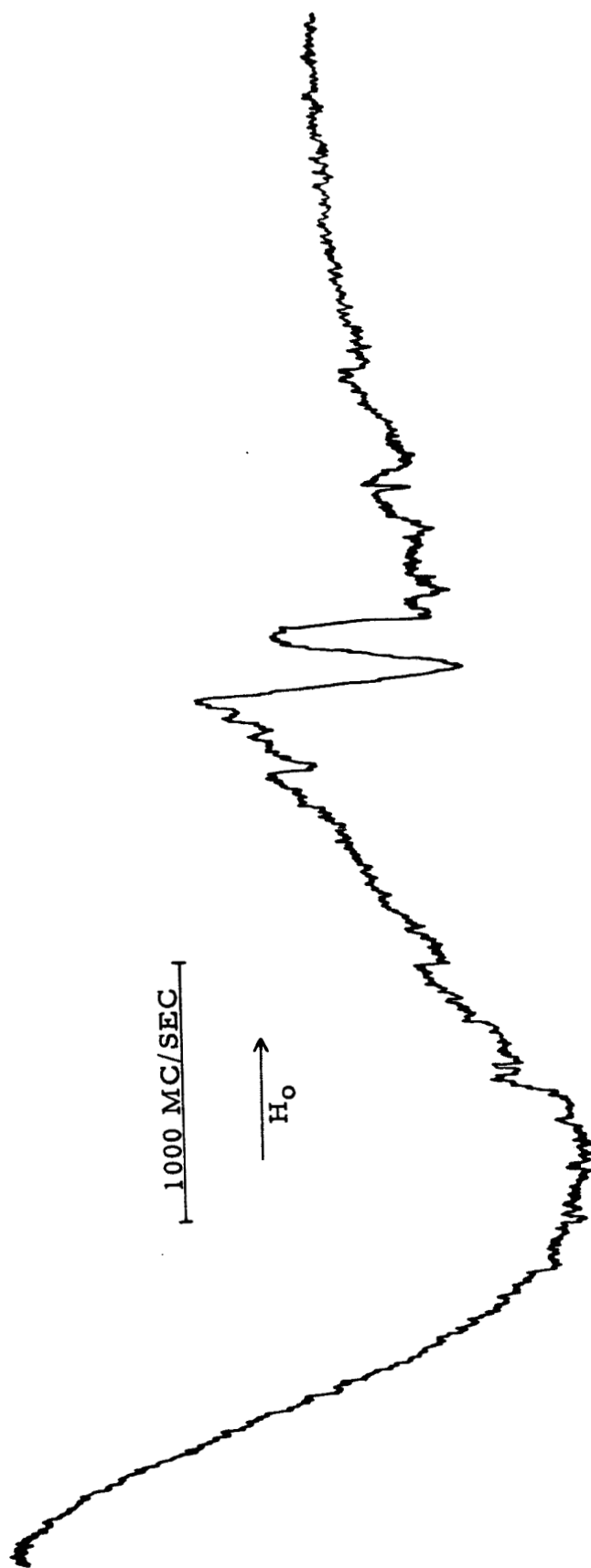


FIGURE 3. ESR SPECTRUM FROM BELL AEROSYSTEMS SAMPLE
 N_2O_4 RESIDUE AT $-196^\circ C$ (BROAD SCAN)

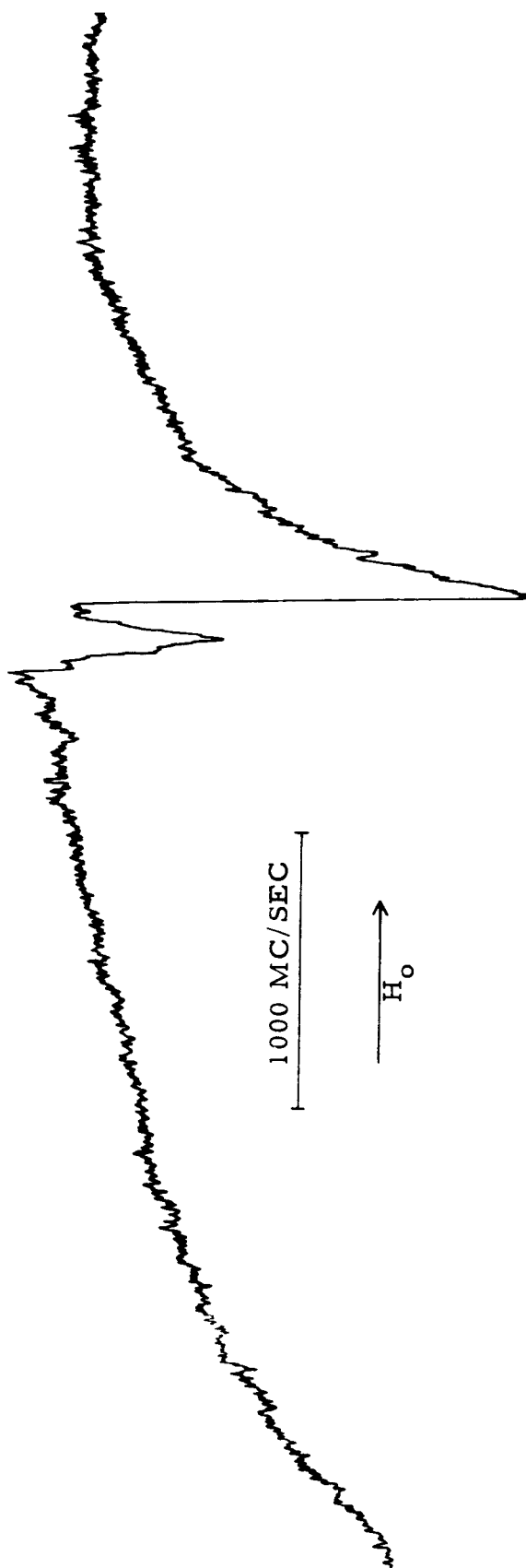


FIGURE 4. ESR SPECTRUM FROM NORTH AMERICAN SAMPLE
 N_2O_4 RESIDUE AT $-196^\circ C$ (BROAD SCAN).

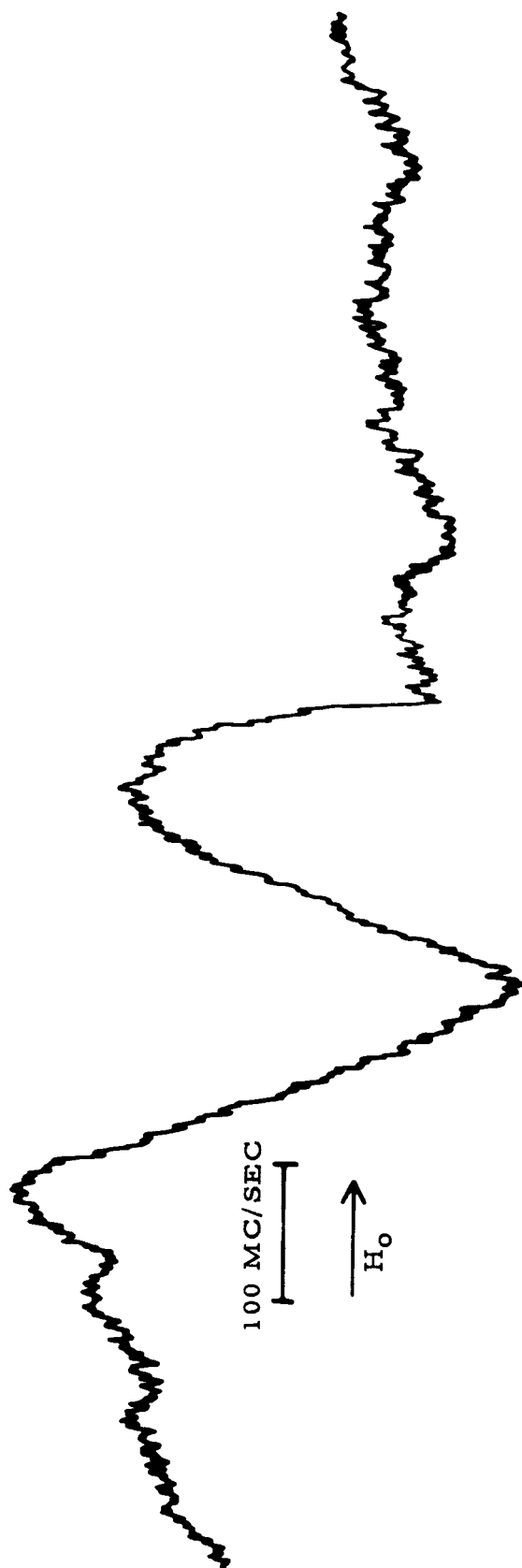


FIGURE 5. ESR SPECTRUM FROM BELL AEROSYSTEMS SAMPLE
 N_2O_4 RESIDUE AT $-196^\circ C$ (NARROW SCAN)

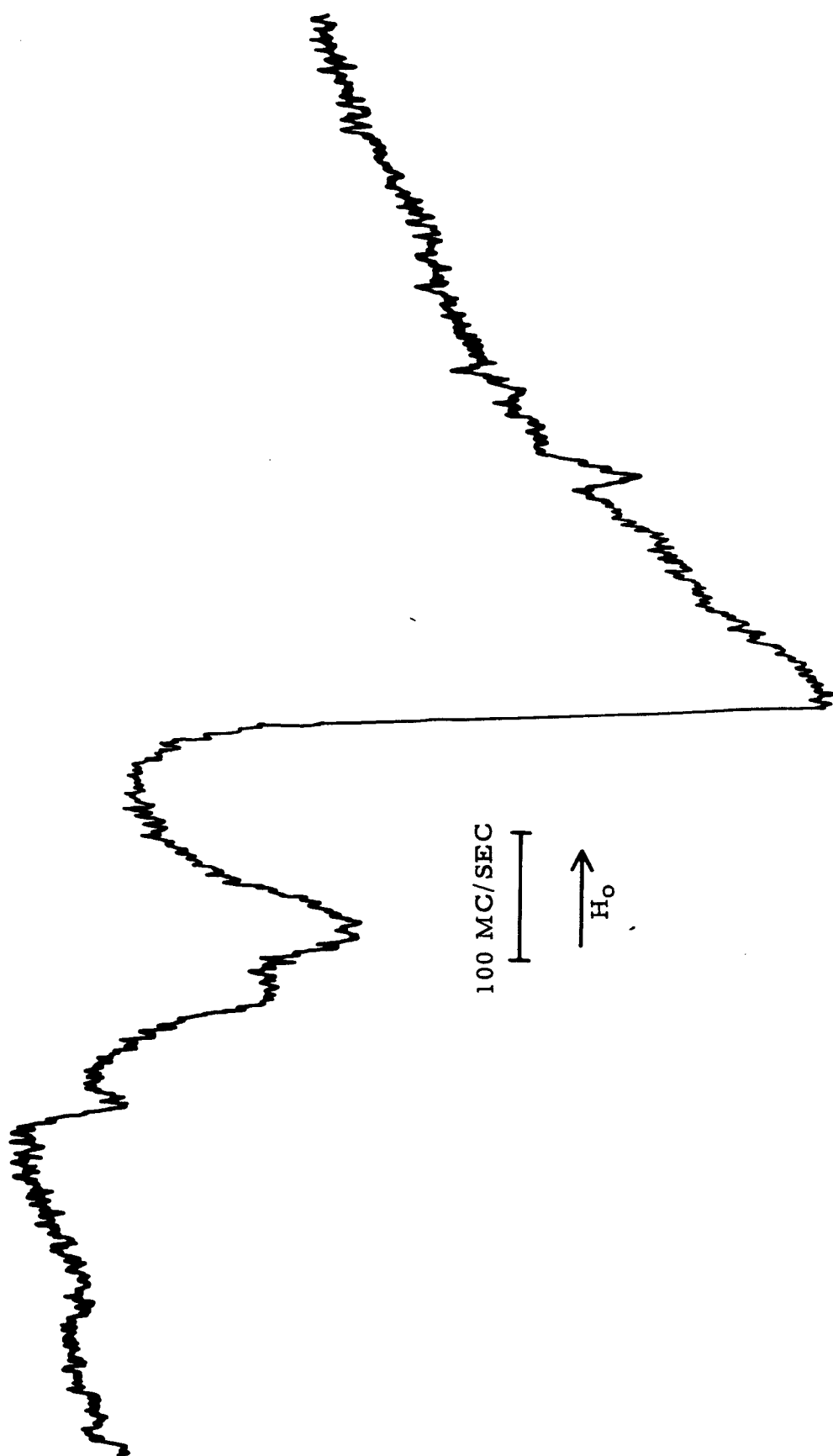


FIGURE 6 ESR SPECTRUM FROM NORTH AMERICAN SAMPLE
 N_2O_4 RESIDUE AT -196°C (NARROW SCAN)

large broad signal at low field which is most probably due to iron. This does not appear in the North American sample. The scans obtained in the region of $g = 2.00$ show differences in the two samples which are most likely due to metal ions. There does not appear to be a significant amount of NO_2 present in these samples. Since better information on metallic constituents was expected from the emission spectrograph analysis, no further attempt was made to identify metals from the ESR spectra. It was concluded that organic constituents did not occur in concentrations that could be detected by ESR.

C. Infrared Absorption

This technique was originally included in the investigation as a possible means of characterizing the organic residue expected. Several evaporation tests were made with the MSC sample, but the amount of residue appeared to be less than one milligram, an amount too small to collect and incorporate into a potassium bromide disc for infrared studies. The water residues obtained with the Bell and North American samples could not be used because of the solubility of potassium bromide in water. Liquid samples could not be used in an infrared cell because of the vapor pressure. Gaseous samples of the N_2O_4 would not show any impurities because of lack of sensitivity. Therefore, further efforts with infrared absorption were abandoned.

D. Gas Chromatography

The technique of gas chromatography utilizes the different adsorption characteristics of gases and vapors to separate them in an adsorption column. In typical applications, a solid column support with a nonvolatile liquid phase is used. Unique characteristics of this method are (1) its ability to separate complex mixtures into their component parts and (2) the ability to obtain data on extremely small samples. This combination of characteristics makes gas chromatography well suited for the measurement of trace impurities if suitable sample preparation methods can be developed.

It was found that the very small amount of residue obtained on evaporation of the N_2O_4 samples was not soluble in any common solvents and therefore could not be introduced into a

chromatographic instrument. An evaluation of instruments, materials, and operating techniques used in past investigations by Southwest Research Institute did not reveal any column materials that would remain active in the presence of N_2O_4 and still separate organic mixtures. Injection of N_2O_4 directly into the instrument likely would not be successful in measuring impurities because of interference from the N_2O_4 . Some consideration was given to passing the N_2O_4 through a separation column of sodium bicarbonate or other alkaline material which might hold back the N_2O_4 and permit the analysis of impurities, but the very small amount of residue present in comparison to the amount of N_2O_4 indicated that this would be difficult or impossible to perform without an extensive study of sample preparation techniques. Therefore, further efforts to utilize gas chromatography were abandoned.

E. Emission Spectrograph

In using this technique, samples are placed in an electric arc and the characteristic emission spectra are recorded photographically. Comparison of the spectra with standard spectra then provides quantitative data on different metallic constituents present.

The nitric acid solutions described previously were evaporated and the solid residue analyzed by emission spectrograph to obtain semiquantitative estimates of any metals present. Table I tabulates the results, calculated on the basis of the concentration of various metals in the original N_2O_4 samples. The major metallic constituent of all samples was silica, but this was due primarily to silica picked up from the crucible used in sample preparation and was not reported. No other significant source of contamination is known, but due to the small amount of residue obtained, some possibility exists that accidental contamination could have occurred. In spite of this difficulty, however, it is believed that the results represent the probable range of concentration of the various metals listed.

The results for aluminum, titanium and vanadium are of interest because of the possible use of N_2O_4 in tanks made of titanium and containing the other two metals as alloying elements. Vanadium was not detected, but a considerable variation was

noted among the four samples in aluminum and titanium. If information could be obtained on the previous history of the samples, these variations might provide clues to differences in corrosion tendencies.

Several other metals also showed significant variations, especially iron. Again, if information were available on the past history of the samples, these variations might provide significant clues concerning corrosion patterns.

TABLE I
METALLIC CONSTITUENTS (EMISSION SPECTROGRAPH)
(Based on original N_2O_4 sample)

	<u>North American</u>	<u>Bell Aerosystems</u>	<u>Hercules Powder</u>	<u>MSC</u>
% Ash in N_2O_4	0.00021	0.00034	0.00014	0.00021
Al, ppm	0.04	0.03	0.008	0.12
B	0.06	0.2	0.1	0.04
Ca	0.01	0.003	0.000006	0.02
Cr	0.00002	0.003	0.00001	0.02
Cu	0.002	0.0007	0.00012	0.006
Fe	0.38	0.14	0.01	0.42
Mg	0.01	0.01	0.005	0.02
Mn	0.00006	0.0001	N. D. (7)	0.00006
Mo	0.02	0.01	N. D.	N. D.
Ni	N. D. (1)	N. D. (4)	0.00004	0.01
Na	N. D. (2)	N. D. (5)	N. D. (8)	N. D. (11)
Ti	0.02	0.003	N. D. (9)	0.01
V	N. D. (3)	N. D. (6)	N. D. (10)	N. D. (12)

N. D. = Not detected

- | | |
|------------------------------------|---------------------------------|
| (1) Limit of detection 0.00006 ppm | (8) Limit of detection 0.001 |
| (2) Limit of detection 0.002 ppm | (9) Limit of detection 0.00003 |
| (3) Limit of detection 0.0001 ppm | (10) Limit of detection 0.00007 |
| (4) Limit of detection 0.0001 | (11) Limit of detection 0.002 |
| (5) Limit of detection 0.003 | (12) Limit of detection 0.0001 |
| (6) Limit of detection 0.0002 | |
| (7) Limit of detection 0.00004 | |

F. Mass Spectrometer

This method was originally intended as a possible means of identifying organic residues. As stated previously, it was later decided to use mass spectrometry in an attempt to measure the amount of nitric oxide in the N_2O_4 samples. Preliminary tests were made with samples of N_2O_4 contained in sealed Pyrex tubes. These tubes were placed in aluminum tubing connected to a sampling inlet of the instrument. The tubing was evacuated and purged after which the tubing was pinched with pliers to break the Pyrex and release the sample. The tubing was then cooled to $28-30^\circ\text{F}$ with ice to reduce the vapor pressure of N_2O_4 and NO_2 and thus concentrate the nitric oxide.

Complete scans were obtained with the four samples in this way and peaks at a mass number of 30 identified as nitric oxide were obtained in all cases. Thus the utility of the mass spectrometer in measuring nitric oxide was demonstrated. However, it was felt that the results were not accurate quantitatively due to interferences in the sample inlet system. Despite evacuation and purging of the system prior to breaking the Pyrex sample tube, it appeared that a residual trace of water and possibly other impurities remained in the metal inlet system. This was shown by the fact that one of the samples, when rerun after 15 minutes, showed less than 50% of the original amount of NO, indicating a probable loss of NO by reaction or absorption in the inlet system. Also, after a period of time, small peaks for sulphur dioxide and carbon dioxide appeared. Since these materials were not thought to be present in the N_2O_4 samples, these peaks likely were anomalies caused by the desorption of these materials which remained in the system from previous hydrocarbon samples which had been analyzed. Since the best cleaning and purging procedures available did not appear to prevent contamination, it was concluded that an all glass inlet system would be required and therefore a complete modification of the sample inlet system and handling procedure was undertaken.

The instrument used in this case was a 21-103C Consolidated Electrodynamics Corporation mass spectrometer. A special borosilicate glass inlet system was constructed, containing no other material except high density teflon valves, and capable of operating at a reduced pressure of 1×10^{-7} Torr or lower. The ionization potential employed was 70 volts from a

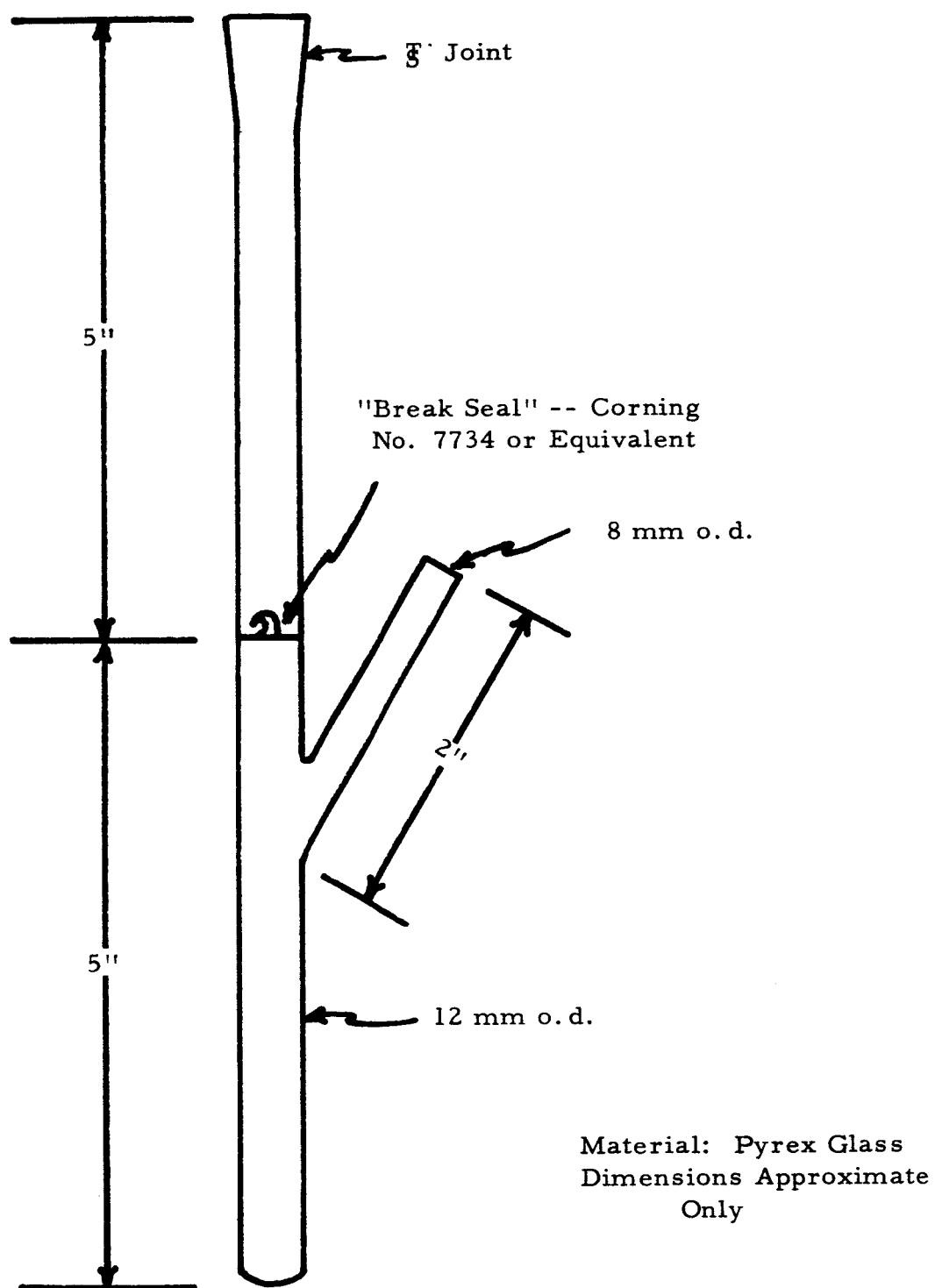


FIGURE 7. SAMPLE CONTAINER FOR VACUUM SYSTEM

rhenum filament assembly which supplied the high energy electrons for ionization of the molecular species present in the N_2O_4 samples.

These instrumental parameters are considered standard for a mass spectrometer operation. The special aspects apply only to the glass inlet system and the method of introduction of the extremely reactive sample materials. It is standard practice to introduce a sample of approximately 100 microns into the instrument, but in this particular case, because of the reactive nature of the samples, it was felt that better results could be obtained by reducing the surface area of the inlet system of the instrument and by increasing the sample pressure. This would reduce the possibilities of reaction, catalytic effects, adsorption, desorption, etc. due to the decreased surface-to-sample ratio. Therefore, an expansion volume of 200 ml was used, which is approximately 1/20 of the regular inlet system volume, and the pressure used was 3,000 microns. Sample data achieved on repeated runs and separate charges of the same samples indicated that these conditions were stable and reliable to obtain meaningful mass spectra. Desorption of materials from the inlet system may have occurred to a very small degree, but was so minute that this would not affect the analytical data.

Another problem was that of obtaining pure nitrogen tetroxide to use as a calibration standard. Attempts were made to prepare such a standard by removing NO from the samples furnished by freezeout or vaporization techniques, but it appeared that the purity achieved in this way did not exceed 97%. Therefore, a calibration standard was obtained from the Matheson Company which was reported to be 99.5% minimum nitrogen tetroxide. A liquid sample from this material appeared to be well above the quoted figure of 99.5% pure, with only minor traces of nitric oxide, nitrogen and oxygen present. These three impurities were eliminated from the spectra in the calculation step to obtain the equivalent spectrum for a supposedly pure sample. This equivalent spectrum was then used as a standard for calculation of all results.

To introduce samples into the instrument without contamination, use was made of a special sample container designed for this purpose, which is illustrated in Figure 7. Approximately 1 ml of liquid nitrogen tetroxide was introduced into the

Typical Mass Spectrum
of
Nitrogen Tetroxide

High Sensitivity Range

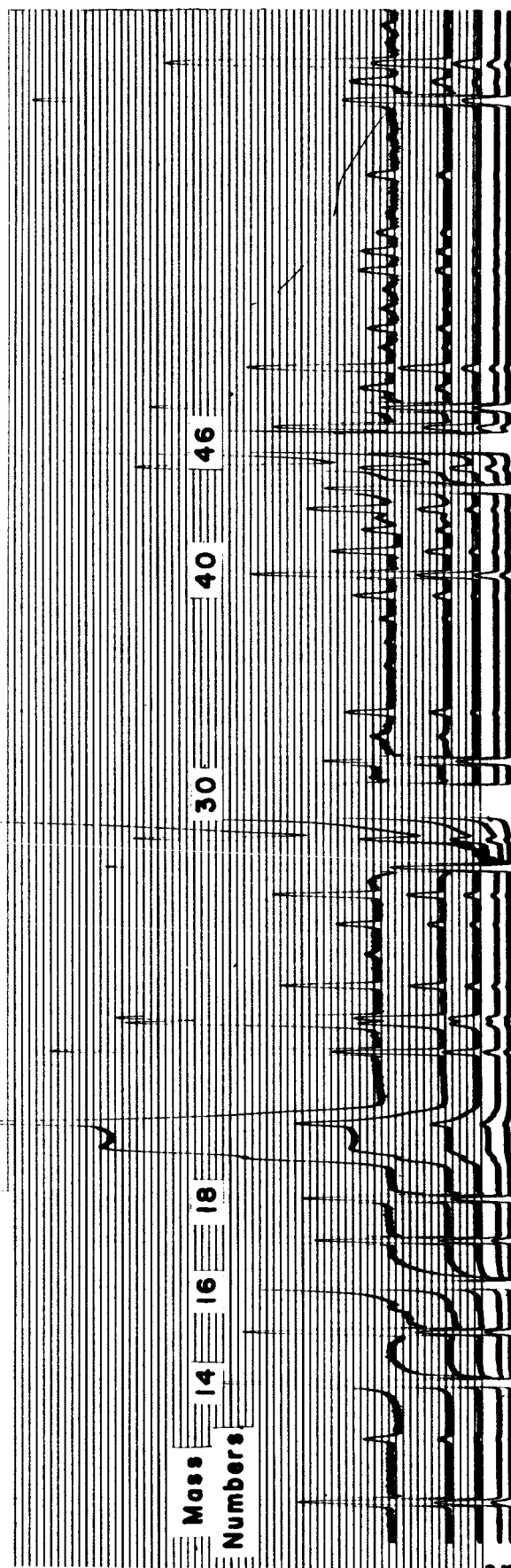


FIGURE 8. TYPICAL MASS SPECTRUM OF NITROGEN TETROXIDE

bottom of the container through the side arm, using the purging procedure described previously. The side arm was then heated with a hand torch and drawn off, thus sealing the sample into the bottom of the sample container. The container was then attached to the special all glass inlet system of the mass spectrometer by the standard taper joint and the upper part of the container and the inlet system were evacuated and purged to remove contaminants. At the time of attaching with the standard taper joint, a small Monel coated magnet was placed carefully on top of the "break seal". After purging and evacuation of the inlet system, this magnet was raised with a steel ring and allowed to fall, fracturing the "break seal" and allowing the nitrogen tetroxide to enter the inlet system of the instrument.

Mass number scans were made with both low and high sensitivity in order to obtain suitable peak heights for all peaks which were significant. Figure 8 shows a typical scan obtained on the high sensitivity range. The five horizontal lines shown are at different sensitivities in the high sensitivity range. The important peaks are shown with the appropriate mass numbers, and are identified as follows:

14	nitrogen
16	oxygen
18	water
30	nitric oxide plus NO fragment from NO ₂
40	argon
46	NO ₂

Other peaks shown are either minor constituents from the sampling system or in most cases represent fragments of NO₂ and possibly NO as a portion of the normal cracking pattern. The fact that the 30 peak represents the sum of the NO present plus a fragment from the 46 peak (NO₂) illustrates the importance of having a standard for calibration purposes that is free of NO. In order to obtain an accurate estimate of NO, the contribution of the NO₂ fragment to the 30 peak must be subtracted, leaving a remainder which measures the amount of NO initially present.

Comparing all peaks in each scan and calculating the total to 100% (mole basis) gave the results indicated in Table II. Nitrogen tetroxide (N_2O_4) and nitrogen dioxide (NO_2) exist in equilibrium and it is thought that the next higher homologue (N_3O_6) may also exist. A 92 peak was not evident, which would correspond to the formula N_2O_4 . This confirms the fact that N_2O_4 is not a distinct molecular species, but N_2O_4 and higher homologues, if they exist, are simply molecular aggregates of NO_2 molecules loosely bound together. Therefore, the value stated for NO_2 is actually the total measure of NO_2 and any higher homologues present.

Nitrogen was the major constituent of all samples because of the use of dry nitrogen as a purge gas to avoid contamination during sample transfer. Most of the nitrogen shown is undoubtedly due to this factor, although some nitrogen probably occurs also as an impurity in nitrogen tetroxide. Oxygen and argon shown are likely impurities from the nitrogen used although, again, minor amounts of these materials might have been dissolved in the original samples. The minor amounts of oxygen and argon make them of relatively little importance.

In view of the extreme precautions in sample handling and the fact that dry residues could be obtained by evaporation of the samples, the introduction of measurable quantities of water during sample handling and transfer seems highly unlikely. Most of the water indicated was likely present in the original samples. This would be expected in view of the nitric oxide shown, since nitric oxide and water exist in equilibrium in nitrogen tetroxide.

In order to provide more realistic figures, the results were recalculated to eliminate the nitrogen, argon and oxygen, on the basis that these constituents were primarily due to the nitrogen purge in handling. The results obtained are shown in the second part of Table II, giving NO_2 , NO , and water values for each sample. The values for NO and water are higher than values obtained by other methods, and therefore, an attempt was made to locate any sources of error.

In the determination of water as specified in Specification MIL-P-26539A, a sample of nitrogen tetroxide is allowed to evaporate and a residue weight is obtained. The water content is then calculated from this weight, on the assumption that the

TABLE II
RESULTS OF MASS SPECTROGRAPH SCANS
(Mole Percent Basis)

A. Original values obtained from scans.

	<u>North American</u>	<u>NASA- MSC</u>	<u>Bell</u>	<u>Hercules</u>
NO ₂	56.02	35.82	33.94	36.24
NO	7.76	3.65	3.65	3.14
O ₂	0.42	0.12	0.06	1.09
A	0.04	0.06	0.31	0.17
H ₂ O	1.23	0.55	0.70	2.21
N ₂	<u>Balance</u>	<u>Balance</u>	<u>Balance</u>	<u>Balance</u>
	100.00	100.00	100.00	100.00

B. Calculated to eliminate N₂, O₂ and A, which were present primarily as a result of nitrogen purging during sample transfer.

	<u>North American</u>	<u>NASA- MSC</u>	<u>Bell</u>	<u>Hercules</u>
NO ₂	86.17	89.51	88.64	87.14
NO	11.94	9.12	9.53	7.55
H ₂ O	<u>1.89</u>	<u>1.37</u>	<u>1.83</u>	<u>5.31</u>
	100.00	100.00	100.00	100.00

residue is 70% nitric acid. However, it would appear that this would give low results, since some loss of water and nitric acid would be expected by vaporization, during the evaporation of the N_2O_4 . Aqueous solutions of nitric acid show measurable partial pressures of both HNO_3 and H_2O ; for example, 70% HNO_3 at 30°C . exhibits partial pressures of 5.50 mm Hg HNO_3 and 7.4 mm Hg H_2O (Perry's Handbook, Fourth Edition). While the chemical reactivity of N_2O_4 and water would undoubtedly alter the pattern of vaporization, it seems likely that measurable amounts of water would be vaporized and removed from the sample during the boiling of N_2O_4 .

The specification does not include any limit on nitric oxide. However, since NO and water contents are interrelated, any change or error in the water content might also affect the indicated concentration of nitric oxide. Therefore, the low values for water and NO as obtained by other methods might be questionable.

Turning now to the results obtained in this study by mass spectrometer, an attempt was made to identify any possible sources of error. The basic principle of measurement appears to be sound, since it involves comparing the pattern obtained with the sample with similar patterns obtained with a high-purity standard. Thus, any decomposition or other change that occurred in the instrument should be duplicated in the standard. Comparing the peaks for mass number 30, which measures NO, it was evident that the samples contained measurable amounts of this material that were not present in the standard. Even allowing for possible errors in calibration, the NO content appeared to be in the range of several percent.

In reviewing the sample preparation and analytical procedures, the only factor which might be open to question was the transfer of N_2O_4 from the original pressure vessel into other sample containers for use in the various analytical procedures employed. Due to the difference in boiling point of N_2O_4 and NO, fractional distillation would be expected if much vaporization occurred during transfer or handling. However, since several analytical tests were to be performed, sample transfer into different containers prior to analysis could not be avoided. An attempt was made to minimize vaporization by cooling the N_2O_4 and this was not thought to be a major source of error. However,

if additional work should be undertaken to measure NO specifically, different procedures might be developed to minimize any possible errors from this source.

With this one exception, any other possible sources of error which are evident would only cause minor changes in the results obtained. For example, absolute accuracy might be affected slightly by the possibility of contamination or some uncertainty in the purity of the calibration standard, but the error should be minor in proportion to the amount of nitric oxide present. Since the calibration standard was claimed to be better than 99.5% pure and since available evidence confirms this claim, any error in the indicated results should be less than 0.2 to 0.4%. Relative error in comparing the NO content of the different samples should be less than 0.1%, based on reproducibility of spectra on different runs with the same sample. This reproducibility would also indicate a sensitivity limit, or minimum detectable amount, of somewhat less than 0.1% NO.

Another source of error which likely can never be completely eliminated with a reactive material such as N_2O_4 is the absorption of atmospheric moisture. Since 100 ml samples could be evaporated without a visible trace of moisture, errors from this source should be negligible in proportion to other possible sources of error.

IV. METHOD OF ANALYSIS FOR NITRIC OXIDE

In the previous section, experimental details were outlined concerning the measurement of nitric oxide in N_2O_4 by mass spectrometer. Important features of this work are outlined here as an aid to the future analysis of NO in N_2O_4 by this method:

1. Some method of sample handling is required to introduce the N_2O_4 into the inlet system of the mass spectrometer. The special sample container developed during this study, featuring the use of a "break seal" device, appeared to be the most feasible method. Others could no doubt be used. Regardless of the exact method used, complete exclusion of all moisture during sample transfer is mandatory.
2. All available evidence indicates that the use of a metal inlet system on the mass spectrometer introduces serious errors. An all glass inlet system can be used to avoid contamination by adsorbed moisture or other impurities. This factor would likely make it impossible to use a mass spectrometer equipped with a metal inlet system. While not mandatory, the use of a smaller volume inlet system at a higher sample pressure than normal, as described previously, increases the analytical sensitivity which can be obtained.
3. The high purity material obtained from Matheson appeared to be suitable as a calibration standard. Further studies of this problem should be made if an attempt were made to further increase the analytical sensitivity for NO.
4. The method as developed in this investigation has a sensitivity, or limit of detection, of approximately 0.1% (mole basis) NO in N_2O_4 . Relative accuracy in comparing different samples should be approximately the same. Absolute accuracy may be no better than 0.2 - 0.4% due to minor errors introduced by trace amounts of NO in the calibration standard. Thus, the method is suitable for measuring NO in the 1% range and above.
5. If better sensitivity and/or accuracy were required, the first priority should be given to obtaining a better calibration

standard. This might be achieved by fractionation of the standard presently available, although this would not be simple to carry out and would require an experimental investigation.

6. Further reduction of the inlet system volume would not be expected to increase sensitivity and/or accuracy to any appreciable degree. Sample pressure cannot be increased above the level used (3000 microns) without hazard to filament life, and at this pressure, further reduction in surface/volume ratio would be undesirable because of the increased possibility of errors due to adsorption and/or reaction.

7. If this method is to be used for the routine analysis of NO in N_2O_4 , additional investigation would be advisable to be sure that vaporization of the sample during transfer and handling does not change the concentration of NO in the samples analyzed. This was not thought to be a problem in the work reported here, but a detailed study of vapor-liquid equilibrium was beyond the scope of this investigation.